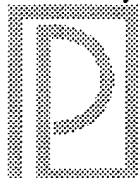


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December 12, 1996

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**VIA HAND-CARRY**

Attention: Examiner S. Hendrickson  
U.S. Patent and Trademark Office  
Group Art Unit: 1103

**GROUP 1100**

Re: U.S. Application of ESCH et al.  
Application No. 08/594,327  
Filed: January 30, 1996  
Group: 1103  
Title: PRECIPITATED SILICAS

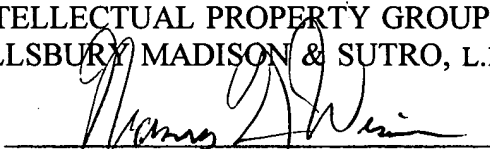
Dear Examiner Hendrickson:

In accordance with your December 4, 1996 telephone discussion with Kevin E. Joyce, Esq., please find enclosed herewith a copy of British Patent Application 2169129. This Application was cited in the Information Disclosure Statement dated August 6, 1996.

Respectfully submitted,

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(54) **Battery separator**

(57) A siliceous filler-reinforced microporous polymeric material battery separator wherein the siliceous filler comprises amorphous, precipitated silica having a specific volume of at least 3.5 cm<sup>3</sup>/g when compacted with an applied pressure of 117 kPa (17 psi), a BET surface area of between about 130 and 180 m<sup>2</sup>/g, an oil absorption of between 200 and 270 millilitres and a median agglomerate particle size of between about 6 and about 15 micrometres (microns). A method for the preparation of the silica is also disclosed.

GB 2 169 129 A

## SPECIFICATION

## Battery separator

- 5 The present invention relates to a siliceous filler-containing battery separator and novel siliceous fillers for use in the preparation of such battery separators. 5

In commonly used electric storage batteries, such as the well-known 12-volt battery employed in automobiles, separators are placed between battery plates of opposite polarity to prevent the two plates from touching each other and causing an electrical short. The separator is typically a

10 microporous article fabricated from a polymeric material, e.g., natural or synthetic rubber, or a polyolefin. The separator may have a backing material of, for example, a non-woven web. The pore size of the microporous separator should be as small as possible since this reduces the danger of active materials being forced through or growing through the separator, thereby causing an electrical short. 10

- 15 The separator should also have a low electrical resistance in order to maximize the power output from the battery. Lower electrical resistance can be obtained by reducing the overall thickness of the separator. However, thinner separators are more subject to corrosion and other physical factors affecting the service life of the separator. 15

- Certain siliceous fillers have been used to prepare microporous battery separators. For example, U.S. Patent Specification No. 2,302,832 describes the use of a silica hydrogel in a rubber binder; U.S. Patent Specification No. 3,351,495 describes synthetic and natural zeolites, precipitated metal silicates, such as calcium silicate, and silica gels as the inorganic filler and extender for separators of high molecular weight polyolefins; and U.S. Patent Specifications Nos. 3,696,061, 4,226,926, and 4,237,083 describe the use of finely divided, precipitated amorphous silica, such as Hi-Sil 233 siliceous pigment, in microporous battery separators (Hi-Sil is a Trade Mark). Hi-Sil 233 amorphous silica is prepared by uninterrupted acidification, e.g., with carbonic acid, of an aqueous solution of sodium silicate to produce a finely-divided powder having a reported BET surface area of between 140 and 160 square metres per gram (see for example, U.S. Patent 2,940,830). 20 25

- 30 Amorphous precipitated silica is used as the vehicle for introducing porosity into and for reinforcing the polymeric material utilized to fabricate the battery separator. Such precipitated silica is highly absorbent and can absorb a substantial quantity of an aqueous or organic liquid while remaining free flowing. In practice, the amorphous precipitated silica is loaded with a liquid of choice, e.g., water or oil, and then blended with the polymeric material. The liquid absorbed by the silica filler is subsequently removed to impart porosity to the polymer. 30 35

- It has now been discovered that certain novel amorphous precipitated silicas permit fabrication of battery separators having reduced electrical resistance compared to separators prepared with conventional amorphous precipitated silica, such as the Hi-Sil 233 silica referred to above. In addition, the precipitated silica of the present invention can be used to provide reinforcement and strength to the polymeric material. Further, the agglomerated particles of precipitated silica of the present invention possess a structure that resists breakage caused by the mechanical stresses to which the silica is subjected during production of the separator. 40 40

- According to the present invention there is provided a siliceous filler-reinforced microporous polymeric material battery separator wherein the siliceous filler comprises amorphous, precipitated silica prepared by the sequential steps of: 45 45

(a) establishing an aqueous solution of alkali metal silicate having an initial alkali metal oxide concentration of from about 5.6 to 7.2 grams per litre and a temperature of between about 88°C and about 92°C (between about 190°F and about 198°F),

- (b) adding slowly to the aqueous solution from step (a) further alkali metal silicate in amounts of from about 2 to about 5 times the amount of alkali metal silicate initially present in the aqueous solution while simultaneously adding acidifying agent to the aqueous solution in amounts sufficient to maintain the alkali metal oxide concentration in the aqueous solution at substantially its initial level, thereby to form an aqueous slurry of siliceous pigment, 50 50

- (c) adding additional acidifying agent to the slurry of step (b) until the pH thereof is from about 8 to about 9, 55 55

(d) ageing the slurry of step (c) at between about 88°C and about 92°C (between about 188°F and about 198°F) for from about 15 to about 90 minutes, and thereafter

(e) adding additional acidifying agent to the slurry of step (d) until the pH thereof is from about 4.0 to about 4.7.

- 60 The present invention also provides amorphous precipitated silica having a specific volume of at least 3.5 cm<sup>3</sup>/g when compacted with an applied pressure of 117 kPa (17 psi), a BET surface area of between about 130 and 180 m<sup>2</sup>/g, an oil absorption of between 200 and 270 millilitres and a median agglomerate particle size of between about 6 and about 15 micrometres (microns). 60

- Amorphous precipitated silica used to produce the reinforced microporous polymeric battery separators of the present invention is prepared by a process involving a sequence of several 65 65

- steps in which the process conditions are carefully controlled. In the first step of the process, a first aqueous solution of alkali metal silicate having an alkali metal oxide concentration of from about 5.6 to 7.2 (e.g., 5.6 to 6.3) grams per litre and a temperature of between about 190°F (88°C) and about 198°F (92°C) is established in a precipitation vessel equipped with agitation
- 5 means. Further alkali metal silicate in an amount equal to from about 2 to about 5 (preferably about 2 to 3) times the amount of alkali metal silicate present in the first aqueous solution is then added slowly to the precipitation vessel while simultaneously adding acidifying agent to the aqueous solution in amounts sufficient to maintain the alkali metal oxide concentration in the first aqueous solution at substantially the same level. Following addition of the further alkali metal
- 10 silicate to the precipitation vessel, additional acidifying agent is added to the resulting slurry until the pH thereof is from about 8 to 9 (preferably about 8.5). This slightly alkaline slurry is then aged at between about 188°F (87°C) and about 198°F (92°C) for from about 15 to about 90 (preferably from about 30 to about 45) minutes. Subsequent to the ageing step, additional acidifying agent is added to the aged slurry until the pH thereof is from about 4.0 to about 4.7.
- 15 The precipitated silica in the acidified slurry can then be recovered, washed and dried. If necessary, the dried product can be milled to break up large agglomerates to obtain a finely divided white product in which the median aggregate particle size is between about 6 and about 15 (preferably between about 8 and about 12) micrometres, as measured by a Coulter counter.
- Any suitable water soluble alkali metal silicate (e.g. sodium silicate) may serve as a source of
- 20 the silica. Such alkali metal silicate may contain from 1 to 5 moles of SiO<sub>2</sub> per mole of alkali metal oxide. Sodium silicate containing from 2 to 4 moles SiO<sub>2</sub> per mole of Na<sub>2</sub>O is a particularly widely available and used material and hence is preferred. Typically, the Na<sub>2</sub>O:SiO<sub>2</sub> ratio is about 1:3.3. Other alkali metal silicates, such as lithium or potassium silicate, may also be used.
- The first aqueous solution of alkali metal silicate, i.e., the solution containing from about 5.6
- 25 to 7.2 grams per litre of alkali metal oxide, is typically prepared by adding an aqueous alkali metal silicate solution, e.g., sodium silicate having a Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 1/3.3, to a predetermined quantity of water heated to between about 190°F (88°C) and about 198°F (92°C) e.g., about 195°F (91°C), in amounts sufficient to establish the desired concentration. This solution is agitated to ensure efficient mixing of the alkali metal silicate added to the water and subsequent
- 30 mixing of the further alkali metal silicate and acidifying agent added thereto.
- In the second step of the process, further alkali metal silicate, and acidifying agent are then added slowly and simultaneously to the first aqueous solution. These are added in relative amounts and at rates sufficient to maintain the alkali metal oxide concentration in the first aqueous solution substantially constant, i.e., at substantially its initial value. Thus, the amount of
- 35 acidifying agent added to the vessel containing the first aqueous alkali metal silicate solution will be slightly less than the stoichiometric amount required for the further alkali metal silicate added to the precipitation vessel so as to compensate for the effect of dilution by the alkali metal silicate and acidifying agent added during the second step. The amount of further alkali metal silicate added is from about 2 to 5 (preferably 2 to 3) times the amount of alkali metal silicate
- 40 initially present in the first aqueous solution.
- The further alkali metal silicate is typically added over a period of from about 60 to 150 minutes, e.g., about 90 minutes. The particular addition time will, of course, depend on the multiple of further alkali metal silicate added, e.g., multiples of 2 to 5. During addition of the further alkali metal silicate and acidifying agent, the temperature of the resulting slurry in the
- 45 precipitation vessel is maintained at about the temperature of the starting alkali metal silicate aqueous solution, e.g., between about 190°F (88°C) and about 198°F (92°C). The further alkali metal silicate added to the precipitation vessel will typically have the same alkali metal cation as the cation of the starting alkali metal silicate solution, e.g., sodium.
- Acidifying agent used to neutralize the alkali metal silicate typically is carbonic acid or an
- 50 inorganic mineral acid, e.g., hydrochloric acid or sulphuric acid. Different acids may be used in the various process steps if desired. The carbonic acid acidifying agent can be furnished by introducing carbon dioxide into the alkali metal silicate aqueous solution. Acidifying agent is added gradually to the precipitation vessel and the amount required is determined by monitoring the pH of the alkali metal silicate solution or slurry in such vessel. The pH can be measured by
- 55 any convenient commercially available pH meter.
- After completing the addition of further alkali metal silicate and acidifying agent to the precipitation vessel, additional acidifying agent is added slowly, and preferably at the same rate used during the preceding (second) process step until the pH of the siliceous slurry is between about 8 and about 9, i.e., slightly alkaline, preferably about 8.5. Thereupon, the slurry is agitated and
- 60 allowed to age at between about 188°F (87°C) and 198°F (92°C), i.e., substantially the temperature maintained during the precipitation step, for from about 15 to about 90 minutes, usually about 30 to about 45 minutes. Following the ageing step, additional acidifying agent is added slowly with agitation to the slurry until the pH thereof reaches between about 4.0 and about 4.7, usually about 4.3 to about 4.7.
- 65 The precipitated silica in the slurry is recovered from the slurry by any suitable solid-liquid

separating means such as a filter press, centrifuge etc. The resulting filter cake can be washed with water to remove water soluble salts, e.g., sodium chloride and/or sodium sulfate. Silica prepared by the above-described method using sulphuric acid as the acidifying agent will typically have a sodium chloride content of less than about 0.10 weight percent, e.g., less than 0.07 weight percent, a sodium sulfate content of less than about 2.5, preferably less than 2.0, weight percent, and a sodium oxide content less than about 1.5 weight percent, e.g., preferably not more than about 1.0 weight percent. The aforesaid values can be determined by X-Ray fluorescence spectroscopy.

Following washing, the filter cake is dried by any suitable drying means, e.g., spray drying, tray and compartment drying, or rotary drying. The dried silica may be used as recovered from the drying step if the particles are sufficiently finely-divided, e.g., such as product recovered from a spray dryer. If, however, the drying step produces large, hard agglomerates or cemented particles, the product can be subjected to a milling or grinding step to produce a more finely-divided product having the appropriate aggregate particle size.

After drying, the silica is a white, fluffy, pulverulent powder that is dry to touch. Despite appearing dry, the silica normally contains water, e.g., between about 2 and 8 percent "free water" by weight. Free water is that which is removed from the silica by heating it at 105°C for 24 hours. The silica also contains "bound water", which refers to that water removed by heating the silica at ignition temperature, i.e., 1000°C to 1200°C for an extended period, e.g., 24 hours. Bound water can constitute between about 2 and 6 percent of the silica. Chemically, the finely-divided, amorphous precipitated hydrated silica contains at least 85, preferably at least 90 and more preferably 93 to 97 weight percent  $\text{SiO}_2$  on an anhydrous basis, i.e., not including free water.

The precipitated silica prepared by the above described process will typically have a BET surface area of between about 130 and 180, (usually about 150) square metres per gram ( $\text{m}^2/\text{g}$ ) and an oil absorption of between about 200 and 270 (preferably between about 230 and about 260) millilitres of oil per hundred grams of silica. In addition, the silica will typically have a water absorption of between about 160 and about 180 millilitres per 100 grams of silica and a median agglomerate particle size of between about 6 and about 15 (preferably between about 8 and about 12) microns (micrometres), as measured by a Coulter counter. The bulk density is usually from about 8 to 12 pounds per cubic foot (12.8–19.2  $\text{kg}/\text{m}^3$ ), e.g., 10 pounds per cubic foot (16  $\text{kg}/\text{m}^3$ ).

The surface area of finely-divided silica can be determined by the method of Brunauer, Emmett and Teller, J. Am. Chem. Soc., 60, 309 (1938). This method, which is often referred to as the BET method, measures the absolute surface area of the material by measuring the amount of gas adsorbed under special conditions of low temperature and pressure. The BET surface areas reported herein were obtained using nitrogen as the gas adsorbed and liquid nitrogen temperatures ( $-196^\circ\text{C}$ ) and at a 0.2 relative pressure. Oil absorption and water absorption values are the volumes of dibutylphthalate oil and water respectively necessary to wet 100 grams of the silica. These values can be obtained using a method like the method described in ASTM D2414-65.

The specific volume of the precipitated silica prepared by the above-described process will be at least 3.5 cubic centimetres per gram ( $\text{cm}^3/\text{g}$ ) (preferably about 3.5 to about 4.7  $\text{cm}^3/\text{g}$  and more preferably 4.0 to 4.7  $\text{cm}^3/\text{g}$ ) when compacted with an applied pressure of 17 pounds per square inch (psi) (117 kPa), and will be at least 2.5  $\text{cm}^3/\text{g}$  (preferably about 2.5 to about 2.7  $\text{cm}^3/\text{g}$ ) when compacted at an applied compaction pressure of 280 psi (1931 kPa).

Compaction of precipitated silica and measurement of the specific volume thereof as a function of the applied pressure is useful for discriminating between different silicas. For example, the specific volume of a silica (which is a value obtained by dividing the sample volume at a given applied pressure by the sample weight) may be correlated to other physical properties of the silica, such as its porosity. Different silicas exhibit unique compaction behaviour as the applied pressure is increased, thereby gradually eliminating the porosity of the silica.

Specific volume measurements, as reported herein, may be calculated using the loading cuve generated by an Instron mechanical testing machine, the sample weight, and dimensions of the die chamber (and hence the sample volume) at any given applied pressure.

The amorphous precipitated silica prepared by the above-described process is a finely-divided solid, particulate material in the form of reinforced flocs or agglomerates of smaller particles of siliceous material. As initially precipitated, amorphous silica is composed of ultrafine, solid spherical particles having an average diameter of about 0.02 microns (micrometres) which appear as strands of beads. These strands collect and intertwine to form a loose aggregate structure with open porosity. In the present invention, the valleys and gaps, i.e., the interstices, of the individual strands are filled in with further silica particles to produce strands having a smoother, e.g., more rod-like appearance. These reinforced, intertwined strands provide a final agglomerate structure which is more resistant to the mechanical forces, i.e., resists being broken down into smaller aggregate structures, applied to it during preparation of the battery separator than non-

reinforced amorphous precipitated silica.

Between about 10 and about 90 weight percent, basis the polymeric material, of the amorphous precipitated silica described hereinabove, is usually used to produce the reinforced microporous polymeric battery separator. Preferably between about 20 and about 75 (more preferably between about 30 and about 60) weight percent of the silica is so used.

The polymeric material into which the silica is incorporated to prepare the microporous battery separator can be any of the conventional natural and synthetic polymeric materials conventionally used to fabricate battery separators. Among such materials, there can be mentioned natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, polyisoprene, high molecular weight olefins such as polyethylene, polypropylene, polybutene, ethylene-propylene copolymers, ethylene-butene copolymers, propylene-butene copolymers, ethylene-propylene-butene copolymers, polyvinyl chloride and vinyl chloride-vinyl acetate copolymers. Mixtures of such materials have also been used to prepare battery separators.

Other conventional materials added to the polymeric material, such as plasticizers, antioxidants, wetting agents, carbon black and curing agents, e.g., sulphur, for rubbery polymeric materials may also be added to the composition used to prepare the battery separator.

Battery separators incorporating the precipitated silica described hereinabove can be prepared in accordance with known techniques for preparing such articles. A typical procedure for preparing a battery separator utilizing a curable rubber is described in U.S. Patent Specification 4,226,926, wherein the siliceous filler is rehydrated to levels of between 65 and 75 percent by admixing the siliceous filler with water. The resulting free flowing rehydrated silica powder is admixed with the polymeric material, e.g., in a Banbury mixer. Thereafter, the mixture (including any additional additives required for curing the polymeric particle) is milled on a 2-roll mill to produce a milled sheet. The milled sheet is soaked in hot water and then calendered for contours. Optionally a backing such as paper or a heat-bonded mat is added to the milled sheet. The calendered sheet is then cut into appropriate sizes.

Another similar procedure is described in U.S. Patent Specification No. 3,351,495, wherein the polymeric material, e.g., a polyolefin having a molecular weight of at least 300,000 is blended with the inert filler, e.g., silica, and a plasticizer. The blend, which may also contain conventional stabilizers or antioxidants, is moulded or shaped, e.g., by extrusion, calendering, injection moulding or compression, into sheets. Plasticizer and/or filler is removed from the sheet by soaking the sheet in a suitable solvent, e.g., chlorinated hydrocarbons for a petroleum oil plasticizer, and water, ethanol, acetone, etc. for a polyethylene glycol plasticizer.

The present invention will now be further described in, but is in no manner limited to the following Examples.

In step (b) the temperature is maintained within plus or minus 1 to 2°F (0.5 to 1°C). In step (c), the heat of reaction and heat of neutralization usually causes a rise in temperature from 2 to 6°F (1 to 3°C), depending on the ambient temperature. Ageing usually results in a loss of 2 to 4°F (1 to 2°C), also depending on the outside ambient temperature where the tank in which ageing is conducted, is located.

#### Example 1

Sodium silicate having an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 3.3 was added with agitation to water heated to 192°F (89°C) in a precipitation vessel until the  $\text{Na}_2\text{O}$  concentration in this first aqueous solution was  $7.0 \pm 0.2$  grams per litre. While maintaining the first aqueous solution at 192°F (89°C), three times the initial volume of sodium silicate and concentrated sulphuric acid were added with agitation over 90 minutes to the precipitation vessel. The rate of acid addition was calculated to maintain the  $\text{Na}_2\text{O}$  concentration in the vessel at about 7.0 grams per litre. When addition of the three additional volumes of sodium silicate was completed, acid addition was continued until the pH of the resulting slurry was about 8.5. Acid addition was then interrupted for 45 minutes to permit the slurry to age. The temperature of the ageing step was 195°F (90.5°C) at the start and 190.6°F (88.1°C) at the end. At the end of the ageing period, concentrated sulphuric acid was added to lower the pH of the slurry to about 4.6. The precipitated silica was filtered and the filter cake washed with water to reduce the level of sodium sulfate by-product salt in the cake to less than 2.5 weight percent. The washed filter cake was refluidized and spray dried. The dried silica was then milled. The product was submitted for physical analysis. Results are tabulated in Table I. The silica was also analyzed for chloride ion, sulfate ion, and sodium ion by X-Ray fluorescence spectroscopy using a model XRD-410 automated X-Ray spectrograph. The spectrograph employs a dual target X-Ray tube (tungsten/chromium) operating at 60 kilovolts and 50 milliamperes for excitation of the minor and trace element spectra.

#### Example 2

The process of Example 1 was repeated except that the temperature of precipitation was 195°F (91°C) and the ageing step temperature was 197.7°F (92.1°C) at the start and 193.9°F

(89.9°C) at the end. Results of analyses of the silica thereby produced are tabulated in Table I.

**Table I**

<u>Silica</u>	<u>OA</u> <sup>1</sup>	<u>H<sub>2</sub>O/A</u> <sup>2</sup>	<u>S.A.</u> <sup>3</sup>	<u>C.C.</u> <sup>4</sup>	<u>F.W.</u> <sup>5</sup>	<u>NaCl,</u> <u>%</u>	<u>Na<sub>2</sub>SO<sub>4</sub></u> <u>%</u>	<u>Na<sub>2</sub>O</u> <u>%</u>
Example 1 <sup>a</sup>	253 <sup>c</sup>	176 <sup>c</sup>	149	12	6.3	.03	1.76	1.37
Example 2	240	158	133	9	N.D.	.06	1.35	0.61
Hi-Sil 233 <sup>b</sup>	200	153	150	13	6	.07	1.8	1.0

1. OA=oil absorption, ml/100 grams

2. H<sub>2</sub>O/A=Water absorption, ml/100 grams

3. S.A.=BET surface area, m<sup>2</sup>/gram

4. C.C.=Coulter counter aggregate particle size, micrometres

5. F.W.=Free water loss at 105°C., percent

a. Average of 5 values

b. Typical analysis

c. Average of 4 values

N.D.—Not determined

The precipitated silica of Example 1 and a Hi-Sil 233 precipitated silica were used to prepare battery separators. The electrical resistance of samples of such battery separators was measured in sulphuric acid (Specific Gravity 1.223) at about room temperature after soaking in the acid for 24 hours to eliminate air bubbles.

The electrical resistance (milliohm-in<sup>2</sup>/mil of thickness) of the battery separator prepared with the Hi-Sil 233 type pigment was found to be 5.00 (average of two samples). By comparison, the electrical resistance of the battery separators prepared with the siliceous filler of Example 1 was 3.77 (average of three values). This represents a reduction in electrical resistance of 1.23 or about 24 percent.

### Example 3

Two samples of precipitated silica sold for use in rubber reinforcement and seven samples of precipitated silica (A–G) prepared in accordance with the process described in the present application were loaded into a cylindrical steel die having an inside diameter of 1.25 inches (3.18 centimetres) and a height of 2.5 inches (6.35 centimetres) on an Instron Model TT mechanical testing machine. The die was filled completely with the silica and gently vibrated to ensure that the die cell was uniformly filled. The loaded silica was continuously compacted at a machine crosshead velocity of 0.02 inch/minute (0.05 centimetre/minute) in the double action mode. A dial indicator measured plunger displacements. The silicas were compacted to a load near 10,000 pounds (4536 Kg), the capacity of the machine, after which the compacted silica samples were unloaded and accurately weighed. The specific volume of each of the silicas was calculated at 17 psi (117 kPa), 280 psi (1931 kPa), 4500 psi (31 MPa), and 8000 psi (55 MPa). Results are tabulated in Table II.

**TABLE II**

5	<u>Silica</u>	Compaction Pressure	Specific Volume				5
			(Pa) (psi)	117kPa <u>17</u>	1931kPa <u>280</u>	31kPa <u>4500</u>	
	Hi-Sil 233		2.967	2.195	1.092	0.851	
10	Hi-Sil 260 <sup>a</sup>		3.361	2.504	1.362	1.131	10
	Ultrasil VN-3 <sup>b</sup>		3.155	1.409	1.270	1.112	
15	A		4.672	--	1.291	1.017	15
	B		3.579	2.489	1.179	0.913	
	C		4.018	2.518	1.152	0.187	
20	D		3.728	2.608	1.325	1.102	20
	E		3.700	2.664	1.320	1.108	
	F		3.688	2.611	1.315	1.103	
25	G		3.967	2.713	1.351	1.061	25

a Precipitated silica with physical properties like Hi-Sil 233.

30 b Silica Product of Degussa Corp. having the following reported properties: BET surface  
area—170 m<sup>2</sup>/g; DBP Oil Absorption—225 ml/100 g; bulk density—15 lb/ft<sup>3</sup> (0.24 gm/cm<sup>3</sup>).  
"Ultrasil" is a Trade Mark. 30

The data of Table II show that the precipitated silica of the present invention, i.e., silica samples  
A—G, have higher specific volumes than the two commercial grades of silica when compacted at  
35 17 psi (117 kPa). Such precipitated silicas, therefore have higher porosity which contributes to  
the improved performance of battery separators prepared with such silicas. As the applied  
pressure is increased and the porosity of the silica is eliminated, the specific volumes are  
lowered accordingly and the differences between the commercial silica samples and those  
prepared by the above-described process are reduced. 40

#### CLAIMS 40

1. A siliceous filler-reinforced microporous polymeric material battery separator wherein the  
siliceous filler comprises amorphous, precipitated silica prepared by the sequential steps of:
  - (a) establishing an aqueous solution of alkali metal silicate having an initial alkali metal oxide  
45 concentration of from about 5.6 to 7.2 grams per litre and a temperature of between about  
88°C and about 92°C (between about 190°F and about 198°F), 45
  - (b) adding slowly to the aqueous solution from step (a) further alkali metal silicate in amounts  
of from about 2 to about 5 times the amount of alkali metal silicate initially present in the  
aqueous solution while simultaneously adding acidifying agent to the aqueous solution in  
50 amounts sufficient to maintain the alkali metal oxide concentration in the aqueous solution at  
substantially its initial level, thereby to form an aqueous slurry of siliceous pigment, 50
  - (c) adding additional acidifying agent to the slurry of step (b) until the pH thereof is from about  
8 to about 9,
  - (d) ageing the slurry of step (c) at between about 88°C and about 92°C (between about 188°F  
55 and about 198°F) for from about 15 to about 90 minutes, and thereafter 55
  - (e) adding additional acidifying agent to the slurry of step (d) until the pH thereof is from about  
4.0 to about 4.7.
2. A battery separator as claimed in claim 1, in which the alkali metal silicate is sodium  
silicate.
- 60 3. A battery separator as claimed in claim 1 or 2, in which the initial alkali metal oxide  
concentration is between about 5.6 and 6.3 grams per litre. 60
4. A battery separator as claimed in claim 1 or 2, in which the initial alkali metal oxide  
concentration is about 7.0 grams per litre.
5. A battery separator as claimed in any of claims 1 to 4, in which the temperature of the  
65 aqueous alkali metal silicate solution of step (a) is about 195°F (91°C). 65



6. A battery separator as claimed in any of claims 1 to 5 in which the further alkali metal silicate added in step (b) is the same alkali metal silicate as in step (a).
7. A battery separator as claimed in any of claims 1 to 6, in which the amount of further alkali metal silicate added in step (b) is from about 2 to 3 times the amount of alkali metal silicate initially present in the solution of step (a). 5
8. A battery separator as claimed in any of claims 1 to 7, in which the acidifying agent in steps (b), (c) and (e) is carbonic acid, hydrochloric acid or sulphuric acid.
9. A battery separator as claimed in claim 8 in which the acidifying agent in steps (b), (c) and (e) is carbonic acid which is introduced as carbon dioxide.
10. A battery separator as claimed in claim 8, in which the acidifying agent in steps (b), (c) and (e) is sulphuric acid. 10
11. A battery separator as claimed in any of claims 1 to 10, in which the pH of the slurry in step (c) is about 8.5.
12. A battery separator as claimed in any of claims 1 to 11, in which the period of ageing of step (d) is from about 30 to about 45 minutes. 15
13. A battery separator as claimed in any of claims 1 to 12, in which, in step (e), additional acidifying agent is added to the slurry of step (d) until the pH thereof is from about 4.3 to about 4.7.
14. A battery separator as claimed in any of claims 1 to 13, in which the precipitated silica of step (e) is recovered from the slurry, washed and dried. 20
15. A battery separator as claimed in claim 14, in which the precipitated silica is dried by spray drying.
16. A battery separator as claimed in claim 14 or 15, in which the dried siliceous pigment is milled to produce a product having a median agglomerate particle size of between about 6 and about 15 micrometres (microns). 25
17. A battery separator as claimed in claim 16, in which the median agglomerate particle size is between about 8 and about 12 micrometres (microns).
18. A battery separator as claimed in any of claims 1 to 17, in which between about 10 and about 90 weight percent of the siliceous filler, basis the polymeric material, is used to prepare the separator. 30
19. A battery separator as claimed in claim 18, in which between about 20 and about 75 weight percent of the siliceous filler, basis the polymeric material, is used to prepare the separator.
20. A battery separator as claimed in claim 19, in which between about 30 and about 60 weight percent of the siliceous filler, basis the polymeric material, is used to prepare the separator. 35
21. A battery separator as claimed in any of claims 1 to 19, in which the polymeric material is selected from natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, polyisoprene, high molecular weight polyethylene, polypropylene, polybutene, ethylene-propylene copolymers, ethylene-butene copolymers, propylene-butene copolymers, ethylene-propylene-butene copolymers, polyvinyl chloride and vinyl chloride-vinyl acetate copolymers. 40
22. A battery separator according to claim 1, substantially as hereinbefore described with reference to any of the Examples.
23. Amorphous precipitated silica having a specific volume of at least 3.5 cm<sup>3</sup>/g when compacted with an applied pressure of 117 kPa (17 psi), a BET surface area of between about 130 and 180 m<sup>2</sup>/g, an oil absorption of between 200 and 270 millilitres and a median agglomerate particle size of between about 6 and about 15 micrometres (microns). 45
24. Amorphous precipitated silica as claimed in claim 23, in which the specific volume is from at least about 3.5 to about 4.7 cm<sup>3</sup>/g.
25. Amorphous precipitated silica as claimed in claim 24 in which the specific volume is from 4.0 to 4.7 cm<sup>3</sup>/g. 50
26. Amorphous precipitated silica as claimed in any of claims 23 to 25, in which the BET surface area is about 150 m<sup>2</sup>/g.
27. Amorphous precipitated silica as claimed in any of claims 23 to 26, in which the oil absorption is between about 230 and about 260 millilitres, and the median agglomerate particle size is between about 8 and about 12 micrometres (microns). 55
28. Amorphous precipitated silica as claimed in any of claims 23 to 27, in which the silica has a bulk density of from about 0.128 to about 0.192 g/cm<sup>3</sup> (about 8 to 12 pounds per cubic foot).
29. Amorphous precipitated silica according to claim 23, substantially as hereinbefore described with particular reference to any of the foregoing Examples. 60

#### CLAIMS

Amendments to the claims have been filed, and have the following effect:—

- 65 Claims 23–29 above have been deleted.

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